**RAPID COMMUNICATION**

# Chiral Heterocyclic Ligands. XIII. Synthesis and X-Ray Crystal Structure of a Chiral, Unidirectional, Silver Coordination Polymer.

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The chiral bridging ligand **2** is shown to react with silver nitrate to produce a new type of chiral coordination polymer with a unidirectional ladder-like structure.

Silver coordination polymers have been the subject of enormous interest in recent years.[1-3] As detailed in the accompanying review,[1] a vast range of one-, two- and three-dimensional metallosupramolecular assemblies have recently been reported, often involving additional weak supramolecular interactions such as hydrogen bonding, π–π stacking or Ag-Ag interactions. Coordination polymers[4-7] are now recognized as offering considerable potential as functional materials.[8-10] One property that has attracted much interest is in the area of non-linear optics (NLO).[11] Certain coordination polymers exhibit interesting NLO properties that may have useful applications in various areas of material science. An important requirement for NLO properties is that the material be non-centrosymmetric. We believe that the simplest approach to the synthesis of non-centrosymmetric coordination polymers is to use chiral bridging ligands.[12] A number of helical silver polymers have been reported using homochiral bridging ligands.[13] Within this context we have previously reported silver(I) and copper(I) coordination polymers derived from the $C_2$-symmetric bridging ligand (**1**) (Figure 1).[14] This bridging ligand was chosen for study because its two N-donors are symmetrically equivalent, thereby avoiding any isomerism complications in self-assembly processes. However, a consequence of this is that the resulting linear chains are necessarily non-directional (Figure 2(a)). It is now recognised that NLO properties can be amplified by directionality, as introduced by polarisation resulting from a less symmetrical bridging ligand (Figure 2(b)).[15]

[Figures 1 and 2 here]

In another context, we have recently reported the syntheses of a number of discrete coordination complexes of the $C_1$-symmetric ligand (**2**), readily available from the common monoterpene camphor.[16] Within these complexes, the ligand acts as a monodentate, rather than bridging, ligand with coordination to the less hindered of the two non-equivalent nitrogen donors. Furthermore, we have recently shown that the common alkaloid (S)-(-)-nicotine can be employed as a synthon for the formation of semi-directional silver coordination polymers.[17] Encouraged by these results, we explored the possibility of using **2** as a bridging ligand for the formation of chiral silver coordination polymers and now report that upon reaction with silver(I) nitrate this ligand faithfully assembles into a unidirectional ladder-like structure, in the solid state.

The silver complex **3** was synthesised from the reaction of **2** with one equivalent of $AgNO_3$ in a 1:1 mixture of acetone-methanol. The crystalline product obtained, in good yield, analysed as [$AgNO_3$(**2**)] by combustion analysis. The crystals isolated from the reaction mixture were too small to permit an X-ray structure analysis, but suitable crystals were obtained from the slow evaporation of an acetonitrile solution of the complex. The compound

crystallises in the monoclinic space group C2, and forms an intriguing metallopolymer in which ligand **2** acts as a bridge using each of its two available nitrogen donors for coordination (Figure 3). The asymmetric unit contains one molecule of **2**, a silver atom and a coordinated nitrate counterion that is disordered over two orientations, with equal occupancies. The two nitrogen atoms of the ligand have very different steric environments, with one (N1) having an adjacent methyl group and the other (N4) an adjacent hydrogen atom. This difference is reflected in the Ag-N bond distances, with the more sterically hindered nitrogen having a longer bond length of 2.28(2) Å compared to 2.18(2) Å for the less hindered nitrogen atom.

[Figure 3 here]

The nitrate anions act as links between adjacent polymer chains thereby producing a 'ladder-like' polymeric structure, as shown in Figure 4. The nitrates are disordered such that each site has either a bidentate bridging oxygen or is non-bridging, with equal probability. Silver atoms bridged by ligand **2** on the sides of the ladder are separated by 7.28(1) Å, while those linked by the nitrate anions on the rungs of the ladder are separated by 4.67(1) Å. Such ladders are well established as a supramolecular motif in silver coordination polymers.[1] Previously reported examples are usually non-directional (Figure 2(c)). However, the present example represents a new type of chiral ladder. The $C_1$-symmetry of the bridging ligand introduces a directional component to the overall architecture of the assembly. Such asymmetry could, in principle, lead to two possible isomeric ladder-like structures: bidirectional (Figure 2(d)) or unidirectional (Figure 2(e)). In the present example the two sides of the ladder are arranged in the same direction (as defined by the orientations of the bridgehead methyl groups), thereby producing what we believe to be the first example of a unidirectional chiral coordination polymer of this type. This situation is allowed by a two-fold rotation axis that is coincident with the axis of propogation of the polymer chain. Furthemore, since the only other symmetry element is a C-centering, all neighbouring ladders are oriented in the same direction.

[Figure 4 here]

In conclusion, we have shown that the $C_1$-symmetric chiral ligand **2** is able to faithfully assemble in a head-to-tail fashion to form polymer chains that are further bridged by nitrate anions to produce a novel chiral unidirectional ladder-like structure.

## Experimental

*Preparation of **3***

Reaction of ligand **2** (19.0mg, 0.1mmol) dissolved in hot acetone with silver nitrate (17.8mg, 0.10mmol) dissolved in hot methanol gave a colourless solution. A crystalline product appeared on standing after 30 mins. Yield 26.4mg (73%). M.p. 274-275°C. Anal. Found: C, 40.24; H, 4.32; N, 11.89. Calc. for $C_{12}H_{16}N_3O_3Ag$: C, 40.24; H, 4.50; N, 11.73. Crystals suitable for X-ray diffraction were obtained by slow evaporation of an acetonitrile solution of the complex.

*X-Ray Crystallography*

Data were collected with a Siemens SMART CCD area detector, using graphite monochromatised Mo Kα radiation (λ = 0.71073 Å). A total of 4048 relections were collected which reduced to 1615 unique reflections ($R_{int}$ = 0.0318). The structure was solved by direct methods using SHELXS,[18] and refined on $F^2$ using all data by full-matrix least-squares procedures with SHELXL-97.[19] The absolute configuration was known from that of the natural starting camphor and confirmed by the Flack parameter[20] of -0.07(10), which showed no evidence of racemic twinning. Hydrogen atoms were included in calculated positions with isotropic displacement parameters 1.3 times the isotropic equivalent of their carrier atoms. The final difference map showed no features greater (or less) than 0.61 e.$Å^{-3}$. Crystallographic data, as a CIF file, have been deposited with the Cambridge Crystallographic Data Centre (CCDC No 286640). Copies can be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (e-mail: deposit@ccdc.cam.ac.uk).

**Crystal data for 3**: $C_{12}H_{16}AgN_3O_3$, MW 358.15, monoclinic, C2, $a$ = 23.853(14), $b$ = 7.279(4), $c$ = 7.284(4) Å, $\beta$ = 94.479(9) $^o$, V = 1260.8(12) $Å^3$, Z = 4, T = -105 $^o$C, F(000) = 720, $\mu$(MoK$\alpha$) = 1.607 $mm^{-1}$, $D_{calcd}$ = 1.887 $g.cm^{-3}$, $2\theta_{max}$ 53 $^o$, 190 parameters, Gof = 1.050, $wR(F^2)$ = 0.0800 (all 1615 data), $wR(F^2)$ = 0.0730 (1348 data with $I > 2\sigma I$), R = 0.0481 (all 1615 data), R = 0.0326 (1348 data with $I > 2\sigma I$).

## Acknowledgement

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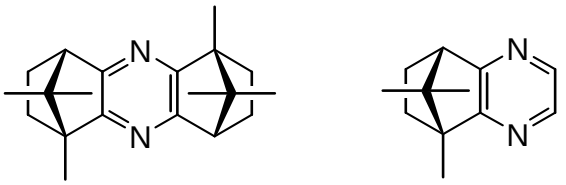


(**1**) (**2**)

**Fig. 1.** Structures of ligands (**1**) and (**2**).

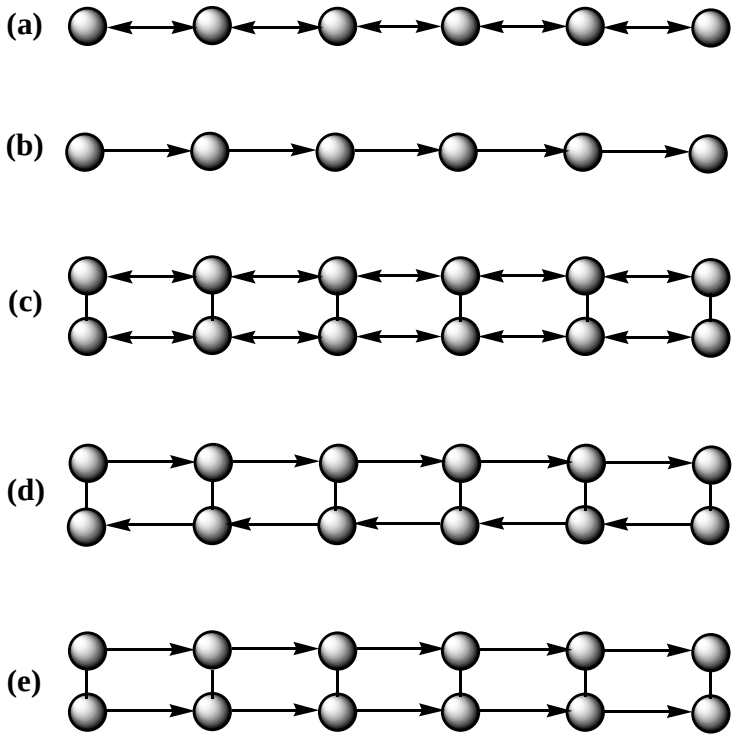


**Fig. 2.** Types of 1-D coordination polymers: (a) non-directional linear chain (b) directional linear chain (c) non-directional ladder (d) bidirectional ladder (c) unidirectional ladder.

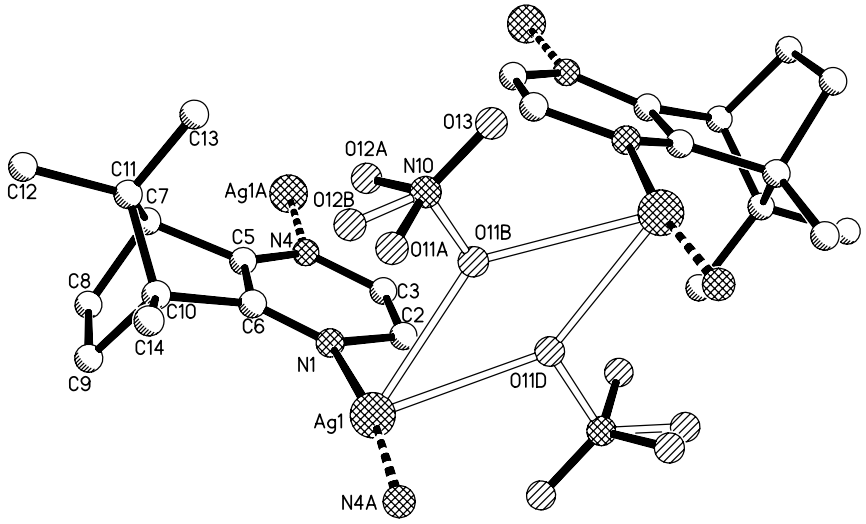


**Fig. 3.** Perspective view of the structure of **3**, showing the disordered nitrate anions. The hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Ag1-N4A$^{i}$ 2.18(2), Ag1-N1 2.28(2), Ag1-O11D$^{ii}$ 2.48(1), Ag1-O11B 2.55(1), N4A$^{i}$-Ag1-N1 173.0(2), N4A$^{i}$-Ag1-O11D$^{ii}$ 96.4(8), N1-Ag1-O11D$^{ii}$ 89.1(8), N4A$^{i}$-Ag1-O11B 96.9(8), N1-Ag1-O11B 90.0(8). Symmetry codes: (i) +x, 1+y, +z (ii) 1-x, +y, -z.

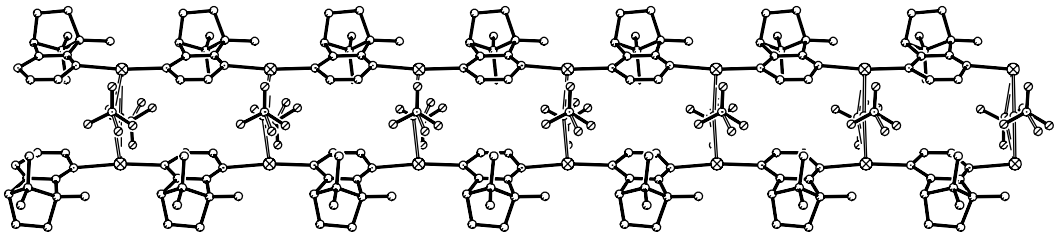

**Fig. 4.** Perspective view of a section of the unidirectional, ladder-like polymeric structure of **3**. The hydrogen atoms have been omitted for clarity.

# Graphical Abstract

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